

THE FRENCH REPUBLIC

National Patent and
Trademark Institute

Paris

11. Publication number:
(Only to be used in copying orders)

2,342,057

PATENT APPLICATION

21.

Number 77 05787

54. **Products Which Create a Physiological Cooling Effect upon Skin and Mucous Membranes**

51. **International Classification:** A 61 K 7/00; C 07 C 69/02//A 23 L 1/22

22. **Filing Date:** February 28, 1977, 3:36 P.M.

33, 32, 31 **Priority Invoked:** *Patent application filed in the Federal Republic of Germany on February 28, 1976, Number P 26 08 226.8, on behalf of the Applicant.*

41. **Date for Availability of Application
to the Public:** *B.O.P.I., "Lists," Number 38, September 23, 1977.*

71. **Applicant:** The company known as HAARMANN & REIMER, G.M.B.H., which is domiciled within the Federal Republic of Germany.

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The present invention pertains to products which create a physiological cooling effect upon skin and mucous membranes.

Menthol, which is the principal ingredient of peppermint essences, is distinguished by a noteworthy cooling effect upon the skin and mucous membranes. Instead of being attributable to latent heat from evaporation, this cooling effect is attributable to direct action by the aforementioned compound upon nerve endings which are receptive to cold. Menthol's olfactory and taste properties limit its use, however, while even rendering use impossible in certain instances. For various areas of application, the peppermint odor is excessively specific and excessively strong, and it may cause tears and irritate mucous membranes. For other areas of application, the taste is excessively strong and bitter. Menthol's high volatility also constitutes a disadvantage in certain instances.

Efforts to identify substances offering a definite cooling effect without menthol's previously described disadvantages have therefore been pursued. Within the first published text of Patent Application Number 2,202,535 in the Federal Republic of Germany, for example, p-menthane-3-carboxamide and esters of p-menthane-3-carboxylic acid were proposed. Within the first published text of Patent Application Number 2,205,255 in the Federal Republic of Germany, p-menthane-3-carboxamides with nitrogen substitution were proposed. Within the first published text of Patent Application Number 2,317,538 in the Federal Republic of Germany, substituted amides were proposed. Within the first published text of Patent Application Number 2,334,985 in the Federal Republic of Germany, sulfoxides and cyclic and acyl sulfones were proposed, and, within the first published text of Patent Application Number 2,345, 156 in the Federal Republic of Germany, substituted phosphinic oxides were proposed.

Compounds which provide the desired cooling effect and closely approach a total absence of odor and taste are nonetheless characterized by a disadvantage: these compounds are not substances of natural origin, and they are not degradable into natural substances within the body. Hence, it is possible to raise questions concerning their safety, and there is a risk of conflict with statutory provisions. Moreover, in certain instances, these are extremely costly products because they can only be prepared by processes involving numerous operating stages.

The previously proposed menthol derivatives, whether they are of natural origin or are degradable into natural substances within the body, only satisfy the indicated needs in an imperfect form. For example, 3-menthyl ethyl-carbonate, which is proposed within the first published text of Patent Application Number 2,022,364 in the Federal Republic of Germany possesses an odor which is reminiscent of oranges. The menthyl ester of N-acetylglycine, which is proposed within the first published text of Patent Application Number 2,433,165 in the Federal Republic of Germany, and menthol esters of heterocyclic carboxylic acids, which are proposed within the first published text of

Patent Application Number 2,339,661 in the Federal Republic of Germany, are bitter. Some of the menthyl ketoesters which are proposed within United States Patent Number 3,830,930 possess a persistent bitter taste and do not provide the desired cooling effect.

The Applicant has determined at this point that, notwithstanding any form of decomposition, menthol esters and hydroxycarboxylic acids of natural origin with C_2-C_6 and with possible esterification of the hydroxy group of the respective acid were odorless and tasteless, while providing a noteworthy and especially persistent cooling effect.

The present invention therefore pertains to products which provide a physiological cooling effect upon skin and mucous membranes, with said products being characterized by the fact that they contain menthol esters and C_2-C_6 hydroxycarboxylic acids of natural origin, with potential esterification of the hydroxy group by means of C_1-C_4 carboxylic acids.

Examples of C_2-C_6 hydroxycarboxylic acids of natural origin which can be cited include glycolic, β -hydroxybutyric, α -hydroxyisovaleric, α -hydroxy- α -methylvaleric, α -hydroxy- γ -methylvaleric, α -hydroxycaproic and β -hydroxycaproic acids, and lactic acid in particular.

Among C_1-C_4 carboxylic acids which may provide esterification of the hydroxy group within hydroxycarboxylic acid, it is possible to cite formic acid, acetic acid, and propionic acid in particular.

Only some of the esters which are to be used in accordance with the invention are new. Among the previously described esters, physiological cooling effects upon skin and mucous membranes have never been cited, however. Esters can be prepared by methods representing the state of the art, such as esterification, catalysis by an acid or by menthol in the instance of hydroxycarboxylic acid, or by reduction of menthyl esters of ketocarboxylic acids. Menthyl ketocarboxylates can be obtained, for example, by transesterification of alkyl ketocarboxylates by means of menthol. Esterification of the hydroxy group within hydroxycarboxylic acid by means of a C_1-C_4 carboxylic acid is preferably completed as a final step.

Esters which are to be used in accordance with the invention possess asymmetrical carbon atoms, and optical isomerism may therefore exist. Depending upon the nature of the initial product and the mode of preparation, it is possible to obtain esters in the form of optical isomers or in the form of pure isomers. The cooling effects of isomers may differ, and a basis may therefore exist for preferring one isomer or another.

Products in accordance with the present invention which are intended to provide a cooling effect can be used in every situation where this particular effect is being sought. For example, it is possible for these products to be introduced into consumable products such as chewing gum, chewing tobacco, cigarettes, beverages, ice cream, candy, etc., pharmaceutical products, personal grooming products, or cosmetic products, such as toothpaste, mouthwash, preparations for gargling, perfumes, powders, lotions, pomades, oils, creams, after-shave lotions, shampoos, etc.

Final products contain sufficient quantities of esters in accordance with the present invention for stimulating cold reception nerve endings and for providing the desired cooling sensation. Usually, a 0.1% to 0.5% proportion of esters in accordance with the invention, in relation to the final product according to weight, is used. In addition to the cooling effect, esters in accordance with the invention, notably menthyl lactate, provide a taste enhancement effect. In other words, they strengthen the taste of other substances which lack flavor. For example, addition of esters in accordance with the present invention, even in smaller quantities than the threshold level for a physiological cooling effect, allow reduction of the amount of peppermint essence, spearmint essence, or other aromatic substances which are to be incorporated within chewing gum, for example, or within mint-flavored toothpaste, without lessening the aroma.

The following examples provide illustrations of the invention without limiting its scope, however. Within these examples, indications of portions and percentages are to be understood in terms of weight, unless stated otherwise.

EXAMPLE 1

Toothpaste

The following ingredients are mixed in the usual manner:

DAB 6 Glycerin	20%
Methyl p-hydroxybenzoate	0.15%
Carboxymethylcellulose	1.2%
Saccharin	0.2%
(Hydrated) dicalcium phosphate	48%
Sodium lauryl sulfate	2.2%
Scenting substance	1.0%
Water	--addition up to 100%

Before completion of the mixing process, 1% 1-menthyl lactate is to be added. This toothpaste is distinguished by its cooling effect.

EXAMPLE 2

Chewing gum

0.3% 1-menthyl 0-acetyl lactate is to be included within a commercial chewing gum base. A wad of chewing gum shall provide a sensation of freshness within the mouth.

EXAMPLE 3Fondant

1% 1-menthyl lactate is to be included within a commercial base for creamy candy. A portion of this candy shall possess an agreeable refreshing taste.

EXAMPLE 4Mouthwash

A concentrated lotion for mouthwash is to be prepared by using the following ingredients:

Ethanol	60%
Bromochlorophene	0.05%
Polyoxyethylene sorbitane monolaurate	1%
Allantoin	0.2%
Saccharin	0.2%
Scenting substance	4.0%
Water	--addition up to 100%

5% 1-menthyl lactate must be added to the mixture. For preparing mouthwash, the concentrate must be diluted with water equivalent to ten times its volume. This mouthwash provides a freshening effect.

A lotion for a mouthwash with the same effect is obtained when the 5% 1-menthyl lactate is replaced with equivalent quantities of 1-menthyl glycolate, β -hydroxybutyrate, α -hydroxyisovalerate, α -hydroxy- α -methylvalerate, α -hydroxy- γ -methylvalerate, α -hydroxycaproate and β -hydroxycaproate.

EXAMPLE 5Facial cleansing lotion

A facial cleansing lotion is to be prepared from the following ingredients:

Ethanol	26.3%
1-menthyl lactate	1%
Scenting substance	0.1%
Emulsifier	4%
1,2-propyleneglycol	1%
Allantoin	0.05%
Lactic acid	0.05%
Water	67.5%

This lotion provides a cooling effect upon facial skin.

EXAMPLE 6After-shave lotion

An after-shave lotion is to be prepared from the following ingredients:

Ethanol	55.5%
1-menthyl lactate	1.5%
Scenting substance	0.5%
Emulsifier	0.3%
Water	39.8%
Allantoin	0.2%
1,2-propyleneglycol	1%
Lactic acid	0.2%

When this lotion is applied to the face, it provides a refreshing effect.

A product with the same effect is obtained when 1-menthyl lactate is replaced with an equivalent amount of 1-menthyl 0-formyl-lactate.

EXAMPLE 7Transparent shampoo

A transparent type of shampoo is prepared from the following ingredients:

Amido-alkyl-betaine from fatty acids	60%
Water	35.3%
Preservation agent	0.2%
d,1-menthyl lactate	2%
Scenting substance	0.5%
Coconut oil diethanolamide	2%

The shampoo provides an intense refreshing effect upon the scalp.

EXAMPLE 8After-bath rubdown lotion

An after-bath rubdown lotion is to be prepared from the following ingredients:

Ethanol	50%
1-menthyl lactate	1.5%
Scenting substance	2%
Lanolin-based lubricant	2%
Emulsifier	1.5%
Water	43%

This lotion shall provide an agreeable refreshing effect.

CLAIMS

1. Products which provide a physiological effect of coolness upon skin and mucous membranes, characterized by the fact that they contain menthol esters and esters of natural C₂-C₆ hydroxycarboxylic acids, which are to be esterified through the hydroxy group by means of C₁-C₄ carboxylic acids.
2. Products in accordance with Claim Number 1, characterized by the fact that they contain menthyl lactate as an active ester.
3. Use of menthol esters and esters of C₂-C₆ hydroxycarboxylic acids which are of natural origin, with said esters to be esterified through the hydroxy group by means of C₁-C₄ carboxylic acids, as products which provide a physiological effect of coolness upon skin and mucous membranes.
4. Use of menthyl lactate in accordance with Claim Number 3.
5. Mixtures containing ingredients which provide an effect of coolness, characterized by the fact that they contain products in accordance with Claims 1 or 2.
6. Mixtures in accordance with Claim Number 5, characterized by the fact that they contain products in accordance with Claim Number 1 or Claim Number 2 in amounts from 0.1% to 5% of total composition according to weight.